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<p>In this presentation, it is shown that noise can be not only a source of difficulty in measurement situations, but can also be used as an information carrier. In most situations, noise serves to obscure signals whose detection is desired. In such situations, it is important to distinguish between additive and multiplicative noise. Additive noise can be overcome by means of conventional signal-processing techniques such as lock-in amplification, signal averaging, and others. In contrast, multiplicative noise can be overcome only through a division-based process such as internal standardization.</p> <p>From another viewpoint, noise can serve nicely as a distinctive information carrier and as a vehicle by which time-dependent phenomena can be measured. This approach has a number of advantages, including signal-to-noise enhancement and the examination of systems which cannot readily be perturbed by pulsed methods.</p>					
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NOISE - FRIEND OR FOE?

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Introduction

Most analytical chemists, indeed a large fraction of laboratory scientists, spend a great deal of their time tracking down noise and attempting to eliminate it. For our purposes here, we will define noise as whatever makes it difficult to obtain a reliable measurement of a signal. From that standpoint, long-term drift and rapid fluctuations in a recorder base line all contribute to instabilities in a signal and hence constitute noise.

As we will see in this brief description, however, noise can also serve as an information carrier. That is, instabilities and fluctuations generated naturally by chemical or other systems can be used to study the systems themselves. In other situations, fluctuations can be intentionally imposed upon a system to be studied, so the system's temporal, chemical, and physical characteristics can be examined.

To put these two seemingly opposite viewpoints into perspective, let us briefly view a typical laboratory instrument from the standpoint of the information which flows through it. We will use here a spectrochemical instrument, although the same approach could be applied to chromatographic, electrochemical, or other analytical instrumentation. The information-theory view of a spectrochemical instrument is diagrammed in Figure 1.

In Figure 1, we see that the main purpose of a chemical instrument is to encode some of the chemical characteristics of the sample into a form that we as human beings can recognize and interpret. In this encoding process, a large number of steps take place. Specifically, we see in Figure 1 that a portion of the information present in the problem to be solved is available in the chemical composition of that sample. This chemical information is then encoded in the sample taken for analysis. In turn, the sample containing this chemical information is introduced into a device we might call the "source" which encodes that same chemical information in the form of the spectral signature of a beam of electromagnetic radiation. To illustrate, the source might be an ultraviolet-visible absorption system, in which a light beam is passed through the sample

to be analyzed. The absorption peaks (the spectral signature) in that transmitted beam can then be used to determine something about the chemical composition of the sample.

For us as human beings to interpret this spectral signature, the various wavelengths or frequencies in the beam of light must be sorted, so the spectral information can be more easily understood. Next, this sorted information is again encoded (by a photodetector), this time in the form of an electronic signal which can be sent to a group of amplifiers, signal modifiers, or signal processors (e.g. a computer) so that the final information is provided in the form of data interpretable by a human being.

This somewhat lengthy and undeniably unconventional view of an analytical instrument helps us recognize how noise can be both an insidious problem and also a benefit. In its most common form, noise can creep into our measurement at any of the steps diagrammed in Figure 1. Whenever an operation occurs to a sample or in a process which serves to encode information about the sample in a different form, noise can corrupt the information and render our interpretation of the resulting signals less reliable. For example, in the process of extracting a chemical sample from the "chemical problem", the wrong sample might be taken, the sample might become contaminated, or the information which the sample provides might be of a kind which is of no value in solving the problem at hand. These uncertainties might all be called "noise".

In a more conventional sense, noise steals into the measurement process in two ways. As shown in Figure 2, noise can be introduced into a measurement step as either an additive or multiplicative component. Noise added to a signal simply makes the signal (or information) seem to fluctuate more or to drift more rapidly. For example, in the ultraviolet-visible absorption measurement mentioned above, such noise might arise from room light which does not pass through the sample. If a UV-visible spectrophotometer leaks light, individuals passing by the instrument will cause the readings to fluctuate in a way that cannot be predicted. These variations then produce inadvertent errors in the reading which can be treated statistically and minimized by a number of signal-processing

approaches which will be mentioned later. Their effects can never be completely overcome, however.

The second form of instrumental noise which is common is multiplicative in its character and in its effect. This kind of instrumental noise can perhaps best be exemplified by events in an ICP emission spectrometer. In such a spectrometer, the intensity of emitted radiation at a desired spectral line is nominally proportional to the concentration of an element in solution responsible for that emission. However, if the nebulizer (sprayer) that feeds the plasma fluctuates, a varying emission signal will be produced whose amplitude is proportional to both the signal magnitude and the nebulizer fluctuation. That is, at a given level of nebulizer variation, twice the element concentration will produce twice the amplitude of fluctuation. This proportionality suggests that the noise is acting in a multiplicative way and therefore cannot be eliminated by simple signal-processing schemes like lock-in amplification and others to be mentioned later. Instead, multiplicative noise can be overcome only by reversing its effect; that is, by division. Thus, when multiplicative noise is present, it can be minimized only through procedures such as internal standardization and isotope dilution; techniques that rely upon dividing the signal from one analyte by that of another. Obviously, for this approach to work requires that the two signals be correlated in their fluctuation.

Many additional examples can be cited for sources of additive and multiplicative noise in chemical processing and chemical instrumentation. For example, drift in the offset or baseline level of an amplifier will be additive whereas drift in the amplifier gain will be multiplicative. Electromagnetic pickup from the 60Hz line or nearby high-frequency equipment (such as an ICP!) will be additive while fluctuation in the primary light source used in fluorescence spectrometry will be multiplicative. It would be an interesting and useful exercise for you to examine the instruments you are now using to determine likely sources of these two kinds of noise.

Elimination of Additive Noise

Because this type of noise is additive, its amplitude is fixed and independent of signal strength. Also, its frequency composition (the frequencies at which it occurs) does not change. As a result, it is often possible to distinguish the signal we desire from noise that accompanies it simply on the basis of the difference in their frequency characteristics. Overall, the feature to remember is that signals are ordinarily controllable or at least coherent (predictable); noise, in contrast, is not.

Because of the importance of its frequency content, noise is often characterized in terms of a *power spectrum*. Common noise power spectra are found in Figure 3.

In Figure 3a, so-called "white noise" is portrayed. As its name suggests, white noise has the same amplitude or power at all frequencies. White noise arises from such things as the discrete nature of photons or charge carriers (electrons, ions, etc.) and from the random motion of charges in a resistor. Although white noise is ubiquitous and cannot be eliminated in ordinary measurements, it is fortunately often of such low amplitude that it does not cause serious problems. If the amplitude of white noise exhibits a Gaussian distribution, it can be treated with conventional statistics.

A second kind of noise, termed $1/f$ because of its spectral shape, is sketched in Figure 3b. Because $1/f$ noise is greatest at low frequencies, it shows up when long-term experiments are performed and is ordinarily termed "drift".

A third type of noise, termed "interference" or "line noise", appears at discrete frequencies and arises from, for example, the 60Hz power line frequency and from other devices.

Ordinarily, noise in a real instrument is a composite of the three types shown in Figure 3. That is, it will contain some white character but will also have contributions from $1/f$ and interference noise. Clearly, then, it is wise to measure signals that are

removed from the noisier regions of a spectrum. It is for this reason that chopping or "modulation" is ordinarily used.

Simply put, modulation permits one to shift the frequency at which a signal is located. Examples of modulation include a chopper placed in a double-beam infrared spectrophotometer or the electronic switching commonly used with hollow cathode lamps.

This "modulation" process places the signal information at a higher frequency, away from dc where $1/f$ noise and drift are greatest. Of course, it requires then a high-frequency detector to recapture the modulated signal. It is for this reason that such devices as frequency-selective or lock-in amplifiers are used for signal recovery.

Alternatively, the signal might naturally or intentionally be pulsed during modulation. If such an approach is used, techniques such as boxcar integration or ensemble averaging can be used. These conventional signal-processing schemes have been described in detail elsewhere (1,2).

From the standpoint of our information-based instrument, the modulation process simply involves encoding the signal information in a slightly different form. If the encoding process is sufficiently unusual (ideally unique), it can be more readily distinguished from noise. Clearly, the decoding process (lock-in amplification, etc.) must then be performed reliably and in a noise-free manner. It is for this reason that a lock-in amplifier, a boxcar integrator, and an ensemble averager require careful synchronization with a modulated or pulsed signal.

A substantial number of additional approaches can be used to aid in the recovery of signals or information buried in additive noise. Correlation and digital filtering techniques (3) are especially important now, since laboratory computers are so readily available. However, no matter how powerful such techniques might be, they do no good against noise which is multiplicative in nature.

Multiplicative Noise and Its Minimization

As stated earlier, multiplicative noise can be overcome only by a division-based process. In short, multiplicative noise works in a manner similar to the modulation process described above. Indeed, multiplicative noise in effect modulates a signal: the result is a noisy signal which fluctuates at the same frequencies as the original multiplicative noise. Because of this frequency similarity, it is impossible to overcome multiplicative noise with the methods outlined in the previous section (1-3).

The only solution to overcoming multiplicative noise is to monitor it and divide the noisy signal by a replica of the noise. As already stated, internal standardization accomplishes just this task. From a broader perspective, however, it should be possible to monitor the primary noise source itself and to remove its contribution from a signal. In the example cited earlier, it might be possible to devise a technique for monitoring fluctuations in the nebulizer that feeds an inductively coupled plasma. If a record of those fluctuations were then kept, they could be used to normalize and therefore correct the fluctuating emission signal that they produce. This normalization, or division, would merely reverse the noise multiplication.

A pitfall in attempting to correct for multiplicative noise often arises when the original noise source is not adequately tracked; that is, when the fluctuating signal and the monitored noise are not coherent. An example here is when an incorrect internal standard is chosen. In such a case, the internal standard fluctuations do not track those of the desired analyte. When this occurs, signal quality might be degraded rather than enhanced by the attempt to correct for the multiplicative effects.

Noise as a Friend

Although it is usually desirable to overcome noise in an analytical measurement, there are times when it can be exploited. Indeed, noise can be a prime information carrier itself.

A simple example can be taken from the fields of photon or ion counting. When a light beam is measured by conventional analog electronics, minute fluctuations in the resulting signal can be attributed to the random arrival of photons. This manifestation of "shot noise" renders the analog signals somewhat unstable and in an unavoidable way. Of course, the photons in such a situation are exactly what should be measured. Consequently, if photon (or ion) counting is employed, the original fluctuations become the signal itself.

Nature provides us with many examples of signals which are fundamentally noisy and where the noise can serve as an information carrier. At small enough levels, matter and energy become discrete, and counting the discrete packets becomes more efficient than attempting to average them. In chemistry, too, we deal on the smallest scale with individual atoms or molecules. If those entities can be measured directly, rather than their average effects monitored, factors which contribute to fundamental measurement noise can be used to learn about the entities themselves.

Consider everyone's favorite chemical reaction, shown in Figure 4. In this reaction, held at macroscopic equilibrium, the molecules of A and B are constantly interacting to produce C, while C is continually dissociating into A and B. If we had available to us instrumentation which could reliably measure individual molecules of C appearing and disappearing, it would register a steady-state trace that would indicate the equilibrium concentration of C. However, superimposed on that steady-state level would be tiny fluctuations that registered the momentary appearance and disappearance of individual C molecules. Importantly, C cannot appear and disappear instantaneously, even though the molecules A and B collide randomly and the random internal forces within C strive to drive it apart. Instead, the formation of C is dictated by the kinetics of the reaction involving A and B while the disappearance of C is rate-limited by the kinetics of its dissociation. Consequently, encoded in the miniscule fluctuations of C that our hypothetical instrument would record are the kinetics of the reaction in Figure 4. An

important remaining question would be how this kinetic information could be extracted from the seemingly random trace that our instrument would produce.

In fact, the kinetic information we desire can be extracted quite easily through techniques such as spectrum analysis and correlation mathematics (3-7). Just as kinetics proceed on a defined time scale, they have a corresponding frequency character. In fact, the two can be related by means of a Fourier transform or power spectrum. For example, if the decomposition of C in Figure 4 proceeded by first-order kinetics, its time behavior would be exponential. The corresponding frequency-domain curve would be Lorentzian in shape. Conveniently for us, this curve can easily be obtained simply by recording the trace from our instrument and obtaining the Fourier transform. Of course, other more sophisticated procedures are also available for such an analysis (3-7).

Clearly, only a few chemical systems can be measured with the sensitivity just described. However, it is possible to extend the same kinds of measurements simply by driving the system being monitored with a bit more force. In the present example, the reaction could be driven back and forth by means of localized pressure fluctuations, since an unequal number of moles exist on the left and right hand sides of the expression in Figure 4. If it is desired for such fluctuations to occur randomly, they might be evoked simply by imposing acoustic noise on the reaction to be monitored. Thus, it should be possible to utilize the same Fourier-transform or correlation approach as before, but instruments of only moderate sensitivity would be required and a greater number of reactions could be examined.

This same kind of scheme can be applied quite broadly. In any instrument where time is an important variable, noise could be used as an intentional driving force. For example, our own work in subnanosecond fluorescence decay measurement (3-5,7) has been carried out using both pulsed and noisy light sources, followed by correlation analysis. Other workers have utilized noisy excitation signals in NMR spectrometry while still others have used a random sample-injection function in chromatography. In all cases,

noise is serving as an information carrier, rather than something which obstructs measurements.

Conclusion

From the foregoing brief discussion, it should be clear that noise and fluctuations are an unavoidable part of any measurement. Additive and multiplicative noise, both very common, require different means for treatment in order to be minimized. In a general scheme, an effort would be made to reduce additive noise, after which a division-based approach would be employed to reduce the effects of multiplicative noise.

However, noise can be a friend also. Because of its broad frequency spread (see Figure 3), noise acts as an exceptional information carrier, especially when time-dependent phenomena are being studied. When used to monitor or perturb chemical systems, noise enables a wide range of new kinds of observations, from the study of kinetics for a reaction *at equilibrium* (6), to the continuous monitoring of a process stream.

Noise can be either a friend or foe. Whichever it is will probably be governed by your knowledge of it and how it can be used.

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Figure Captions

1. Information-theory view of a spectrochemical instrument. Other analytical instrumentation could also be viewed from a similar perspective. See text for discussion.
2. Schematic illustration of additive and multiplicative noise and their effect. Multiplicative noise N_1 appears to have an effect that is proportional to the signal S itself and might be generated by, for example, a fluctuating nebulizer in ICP emission spectrometry or by drift in an amplifier gain. Noise source N_2 is additive and could arise from a number of sources, including amplifier offset drift and leakage of room light into a spectrometer.
3. Noise power spectra. (a) white noise; (b) $1/f$ noise; (c) line or "interference" noise.
4. A typical reaction at equilibrium. Under extremely close scrutiny, the reaction will exhibit tiny fluctuations from its equilibrium position; the temporal record of these fluctuations, although they appear noisy, have hidden in them information about the forward and reverse kinetics of the reaction.







